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Physica C 426–431 (2005) 426–430
PHYSICA C
www.elsevier.com/locate/physc

Synthesizing nanocrystals of metal di-chalcogenide charge density wave system

T. Toshima *, S. Tanda

Department of Applied Physics, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8 Kita-ku, Sapporo 060-8628, Japan

Received 23 November 2004; accepted 22 March 2005
Available online 26 July 2005

Abstract

We have studied charge density wave (CDW) in low-dimensional conductors, metal tri-chalcogenides (MX_3), and metal di-chalcogenides (MX_2). The Fröhlich superconductivity is achieved through an ideal system in the absence of pinning potential. Downsizing is a promising approach. We succeeded in synthesizing $TaSe_2$ nanocrystals by the *de-chalcogenide method*. $TaSe_2$ crystals were obtained by the hydrogen reduction of $TaSe_3$ nanofibers at a relatively low temperature (300 °C). Therefore, we propose a conversion mechanism to obtain $TaSe_2$ from $TaSe_3$ by the de-chalcogenide method. The $TaSe_2$ nanocrystals thus obtained were investigated by transmission electron microscopy and electron diffraction, and new CDW phases ($\sqrt{26.21} \times \sqrt{26.21}$, $\sqrt{7} \times \sqrt{7}$, and 2×2 superlattices) were discovered.

PACS: 71.45.L; 68.55

Keywords: Fröhlich superconductivity; Charge density wave; Thin films

1. Introduction

The Fröhlich superconductivity theory [1] predicted a zero resistance system before the BCS theory [2] was proposed. According to this theory, the electrons of low-dimensional systems form a charge density wave (CDW) [3–5] originating from Peierls instability, and the collective motion of CDW carries electric current by changing its phase without any resistance. Few drawbacks associated with Fröhlich superconductivity are that pinning potential originating from the lattice defects, impurities and commensurability energy of lattice, and charge density wavelength are not taken into account. In particular, the lattice defects and impurities also form the dissipation sources. Ideally, a

* Corresponding author. Tel./fax: +81 011 706 7293.
E-mail address: toshima@eng.hokudai.ac.jp (T. Toshima).

0921-4534/$ - see front matter
doi:10.1016/j.physc.2005.03.070

pure monolayer crystal with incommensurate-CDW phase is required to realize the Fröhlich superconductivity. The purity of crystals is dependent on the system size. When the system size is decreased, the number of pinning sources decreases. Mechanical (Focused Ion Beam) techniques decrease the area of the system size of area, and chemical (intercalation) techniques decrease interaction between one layer and the other layer, which is equivalent to monolayer (strengthened two-dimensionality). However, these methods cannot be applied to the system simultaneously, because this will lead to the infiltration of other pinning sources into the system. Hence, another method is required to downsize the CDW system for achieving a smaller system size and reduced interaction of non-two-dimensionality.

Here we report a novel synthesizing method the *de-chalcogenide method*. Tantalum triselenide ($TaSe_3$) crystals are used as a template. The de-chalcogenide method synthesizes tantalum diselenide ($TaSe_2$) CDW crystals on the surface of the $TaSe_3$ crystals. We observed these crystals using a transmission electron microscope (TEM) and a transmission electron diffraction (TED). The charge density wavelength of the nanocrystals was modified according to the wavelength of the bulk sample.

2. Experimental

We synthesized single crystals of $TaSe_3$ by the conventional chemical vapor transport (CVT) method [6]. A mixture of baked tantalum and selenium powders (purify $3N^+$) was introduced into an evacuated quartz tube. The vacuum in the tube was approximately 10–6 Torr. The quartz tube was heated in an electric furnace from room temperature to 700 °C at a rate of 10 °C/min with a temperature gradient of 1/cm (higher area at 700 °C, lower area at 680 °C). The reaction time was approximately 3–5 h. After the reaction, one end of the tube was quenched using liquid nitrogen to block the clinging of the unreacted selenium gas on the synthesized $TaSe_3$ crystals. The other end of the tube was cut open in vacuum. The $TaSe_3$ crystals were approximately 10–1.0 mm in width and thickness and 100–10 mm in length.

We used these crystals as a template to crystallize the $TaSe_2$ nanocrystals. $TaSe_3$ crystals were placed on a quartz sheet and set in an electric furnace Thermo Riko IVF298. The sample chamber was evacuated using rotary and diffusion pumps to 10–5 Torr, and then it was occasionally permuted with hydrogen gas to remove the oxygen gas from the sample chamber because oxygen atoms get easily activated with tantalum, $TaSe_3$, and $TaSe_2$ at high temperatures. Next, $TaSe_3$ crystals were rapidly heated to approximately 300 °C with a hydrogen gas flow of 1 sccm. During this reaction, the vacuum of the sample chamber was maintained at approximately 10–3 Torr. The chemical reaction time was 30 min. After the reaction, $TaSe_3$ crystals were cooled to room temperature with a hydrogen gas flow. $TaSe_2$ nanocrystals were crystallized on the surface of $TaSe_3$ by the reaction that can be represented as: $TaSe_3 + H_2\,(gas) \rightarrow TaSe_2 + H_2Se\,(gas)$. These crystals were sonicated in isopropyl alcohol for 30 min and allowed to stand for 1 h in order to make the large crystals settle for observation. The surface isopropyl alcohol was collected to study these nanocrystals, which were subsequently placed on the substrate. We then used TEM and TED to investigate these crystals on the substrate.

3. Result and discussion

Fig. 1(a) is a TEM image of a $TaSe_2$ nanocrystal on the $TaSe_3$ nanofiber. Results suggest that hexagonal plate-like $TaSe_2$ grows on needle-like $TaSe_3$. The identification of two other crystal habits provides evidence of the presence of other crystal growth conditions. The width of $TaSe_2$ and $TaSe_3$ is of the same order (approximately 40 nm). However, the thickness of $TaSe_2$ is smaller than that of $TaSe_3$, i.e., the thickness of the $TaSe_2$ nanocrystal is estimated to be approximately 10 nm or less, while that of the $TaSe_3$ is estimated to be approximately 40 nm. This result suggests that $TaSe_2$ crystals may be smaller than the template size. Fig. 1(b) is a simple model of the de-chalcogenide method. Surface three layers are Se–Ta–Se, $TaSe_2$ monolayer. Inner atoms are $TaSe_3$ chains, which is looked from *b*-chain.